Use of ICP/MS with Ultrasonic Nebulizer for Routine Determination of Uranium Activity Ratios in Natural Water

THOMAS F. KRAEMER,*,†
MICHAEL W. DOUGHTEN,‡ AND
THOMAS D. BULLEN§

Mail Stop 430, U.S. Geological Survey, 12201 Sunrise Valley Drive, Reston, Virginia 20192, Mail Stop 432, U.S. Geological Survey, 12201 Sunrise Valley Drive, Reston, Virginia 20192, and Building 15, McKelvey Building, U.S. Geological Survey, Menlo Park, California 94025

A method is described that allows precise determination of $^{234}U/^{238}U$ activity ratios (UAR) in most natural waters using commonly available inductively coupled plasma/mass spectrometry (ICP/MS) instrumentation and accessories. The precision achieved by this technique (±0.5% RSD, 1 sigma) is intermediate between thermal ionization mass spectrometry (±0.25% RSD, 1 sigma) and alpha particle spectrometry (±5% RSD, 1 sigma). It is precise and rapid enough to allow analysis of a large number of samples in a short period of time at low cost using standard, commercially available quadrupole instrumentation with ultrasonic nebulizer and desolvator accessories. UARs have been analyzed successfully in fresh to moderately saline waters with U concentrations of from less than 1 μg/L to nearly 100 μg/L. An example of the uses of these data is shown for a study of surface-water mixing in the North Platte River in western Nebraska. This rapid and easy technique should encourage the wider use of uranium isotopes in surface-water and groundwater investigations, both for qualitative (e.g. identifying sources of water) and quantitative (e.g. determining end-member mixing ratios purposes.

Introduction

Uranium isotopes have been used in hydrologic and environmental studies since the 1960s as a means of evaluating weathering processes, estimating water mixing ratios, and identifying water sources (see, for example, refs *1* and *2*). The usefulness of dissolved uranium isotopes lies in the slight fractionation of ^{234}U over ^{238}U that occurs during weathering, whereby the process of alpha decay causes physical and chemical changes in host material, making the ^{234}U decay product more susceptible to leaching and removal than the parent ^{238}U (*3*). As a result, the activity of ^{234}U commonly exceeds the activity of ^{238}U in water, resulting in a $^{234}U/^{238}U$ activity ratio (UAR) higher than the equilibrium value of 1.000 found in a closed system. Waters contained in diverse rock environments can therefore acquire distinct UARs, enabling

them to be subsequently identified as they emerge and move as surface water or groundwater.

These UARs then can become tracers that can be used as an additional tool to be applied to environmental problems by, for example, identifying source areas of water containing contaminant materials or helping to predict future transport of a contaminant based on establishing the present flow path of groundwater. There is also the direct application to areas where naturally high uranium concentrations in water limits its use due to concern for human health, such as exceeding maximum contaminant levels for drinking water. Uranium isotopes could reveal sources of the uranium or processes that cause it to exceed the limits and enable possible alternate sources to be located.

Despite showing utility in these areas, lack of precision and the large sample size requirement of alpha particle spectroscopy and the high expense and technical skill requirements of the more recently applied, highly precise thermal ionization mass spectrometry method (TIMS) have been major obstacles to the full use of these isotopes in the fields of hydrology and environmental science. The advent of inductively coupled plasma/mass spectrometry (ICP/MS) offers a middle ground between these two methods, whereby an isotopic ratio of high precision can be obtained (*4,5*) while taking advantage of the high sample through-put offered by ICP/MS.

ICP/MS instrumentation has been developed for isotopic determinations of elements that encompasses a broad range of technology, including double-focusing magnetic sector field ICP/MS with single or multiple collectors and various types of injection systems that can approach thermal ionization mass spectrometry (TIMS) precision (*4, 6−10*). Although these types of ICP/MS instrumentation require less sample preparation and less time per analysis than TIMS, they are relatively expensive and of limited availability. More basic, lower precision quadrupole instruments have been used to obtain isotopic ratios where the need for ultimate precision is not paramount, and many isotopic determinations of uranium reported in the literature as having been done by ICP/MS techniques have been performed using quadrupole instrumentation. For example, ^{234}U, ^{235}U, and ^{238}U have been measured in soils (*5, 11*) and in particulate matter collected from atmospheric air filters (*12*), all on standard quadrupole ICP/MS instruments following sample dissolution and processing. Preconcentration techniques using an ion-exchange flow injection autosampler manifold system and ultrasonic nebulizer were used to enhance sensitivity of the $^{234}U^+$ ion signal (*5*). None of these studies reported determination of the ^{234}U in solid samples to better than about 1% (1-sigma RSD) absolute ^{234}U, or 5% $^{234}U/^{238}U$, which was about equal to that which could be achieved by alpha spectrometry. The above-mentioned determinations were made on particulate matter, where the concentration of uranium is typically one thousand times higher (μg/g) than is expected in natural waters (μg/L).

Outstanding precision (0.5%, 2-sigma RSD) for UARs in natural water and carbonates has been achieved using a standard quadrupole ICP/MS, and this technique was shown to have applications in hydrology and geology (*13*). The technique, however, required extremely high uranium concentrations (up to 25 ppm U), a nonstandard sample delivery system using a recirculating nebulizer and long analytical times per sample (1 to 3 h) as the sample solution was continuously cycled into the spray chamber, collected, and reinjected. These requirements placed severe limitations on the technique as a way of analyzing a large number

* Corresponding author phone: (703)648-5868; fax: (703)648-5484; e-mail: Tkraemer@usgs.gov.
† Mail Stop 430, U.S. Geological Survey.
‡ Mail Stop 432, U.S. Geological Survey.
§ Building 15, McKelvey Building, U.S. Geological Survey.

of samples in a quick and efficient manner.

We report here a method for determining UARs using a quadrupole instrument whose only modification is the attachment of a commercially available ultrasonic nebulizer and desolvator for enhanced sensitivity. The precision attained by this method is ±0.5% RSD (1 sigma) on a routine basis, intermediate between alpha spectroscopy and TIMS.

Experimental Section

A Perkin-Elmer ELAN 6000 ICP/MS with CETAC U-6000 AT+ ultrasonic nebulizer and CETAC membrane desolvator (model MDX-200) were used in this study as supplied by the manufacturer without additional modification.

The operational approach to the analysis was to measure the $^{234}U^+$ and $^{235}U^+$ ion intensities rather than try to measure the extreme differences in $^{234}U^+$ and $^{238}U^+$ ion intensities that would occur in a natural uranium sample. By measuring the $^{234}U^+$ and $^{235}U^+$ intensities, the detector could be kept in the pulse mode for both measurements, rather than shifting back and forth between pulse mode for $^{234}U^+$ measurement and analogue mode for $^{238}U^+$ measurement; it was theorized that the most precise ratios could be determined in this way. This is supported by the fact that when we used the "customized resolution" feature of the Elan 6000 to reduce the $^{238}U^+$ ion intensity so that direct comparison of $^{234}U^+$ and $^{238}U^+$ could be achieved, the RSD of the isotopic analysis degraded to well over 2% RSD (1 sigma) in most cases. This was probably the result of sampling the $^{238}U^+$ peak at too few locations to achieve maximum precision.

The $^{235}U/^{238}U$ mass ratio is essentially invariant in natural uranium, and it was assumed there was no variation in the sample from that reported in the literature (*14*) of 7.253×10^{-3}. The $^{234}U/^{238}U$ activity ratio (UAR) of a sample could then be calculated

$$\mathrm{UAR}_{\mathrm{samp}} = \frac{\left[\frac{^{234}U}{^{235}U}\right]_{\mathrm{samp}} \left[\frac{^{235}U}{^{238}U}\right]_{N}}{\left[\frac{^{234}U}{^{238}U}\right]_{N}} \qquad (1)$$

where $[^{234}U/^{235}U]_{\mathrm{samp}}$ is the mass ratio of ^{234}U to ^{235}U measured for the sample, $[^{235}U/^{238}U]_{N}$ is the mass ratio of ^{235}U to ^{238}U (7.253×10^{-3}) for natural uranium, and $[^{234}U/^{238}U]_{N}$ is the mass ratio of ^{234}U to ^{238}U (5.591×10^{-5}) for natural uranium in secular equilibrium. The values chosen for the natural ratios are based on published data (*14*).

Optimal operational performance of the instrument was determined by running NIST 4321B (Natural Uranium Standard). This standard was chosen because it is easily available and has an adequately known UAR (0.963±0.003) (*15*), making it an ideal standard to use in keeping with the objective of making the technique useable by most laboratories.

The overall objective of the optimization process was to maximize $^{234}U^+$ ion count rate while minimizing sample consumption. NIST 4321B was introduced into the instrument through the ultrasonic nebulizer/desolvator while varying operational parameters until each achieved maximum $^{234}U^+$ signal output. Dilutions of NIST 4321B of 50 μg/L and 100 μg/L were used to measure both the response in signal strength and mass discrimination effect exhibited by the instrument at high mass range. The magnitude of the mass discrimination factor was determined to be less than 2% ($^{234}U^+$ being under-counted relative to $^{238}U^+$) based on the NIST-supplied data with the standards certificate. The average UAR based on 19 replicates of the standard (both the 50- and 100 μg/L solutions) run as a sample after the instrument had been standardized to a $^{234}U/^{235}U$ mass ratio of 7.359×10^{-3} was 0.966 with an RSD of 0.34% (1 sigma).

TABLE 1. ICP/MS Instrument Operating Conditions for $^{234}U/^{235}U$ Isotopic Determination Mode

|	
nebulizer flow	0.65 L/min
lens voltage	7 V
plasma RF power	1000 W
dead time	55 ns
sweeps	150
replicates	5
dwell time ^{234}U	100 ms
dwell time ^{235}U	100 ms
peak processing mode	averaged
scanning mode	peak hopping
detector mode	pulse only
sample introduction rate	2.0 mL/min
vacuum	$\sim$2.7 $\times$ 10^{-5} Torr
ultrasonic nebulizer heater temperature	140 °C
cooler temperature	3 °C
desolvator heater temperature	160 °C
sweep gas flow	1.6 L/min
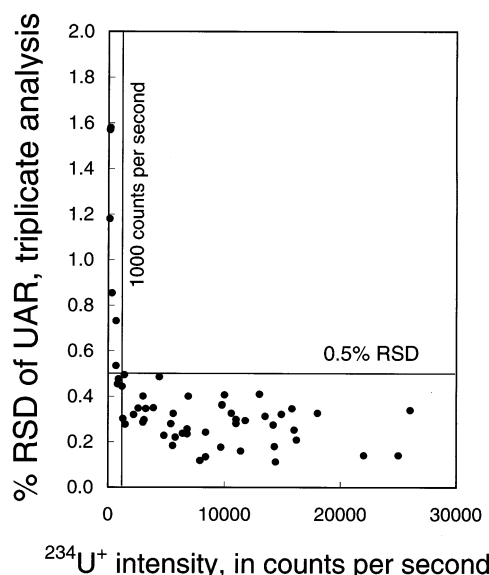
FIGURE 1. Percent relative standard error for UAR determination on samples run in triplicate according to technique described in text. Method produces a 0.5% RSD or less for $^{234}U^+$ count rates of 1000 cps or above.

This is within the 1−sigma error reported for the standard and indicated that the instrument could perform acceptable uranium isotopic determinations. The operating parameters that produced the highest stable $^{234}U^+$ ion count rates during optimization of the instrument are shown in Table 1.

After establishing that the instrument could reach the necessary sensitivity in producing isotope ratio results, the ICP/MS instrument behavior was investigated for its ability to supply accurate UAR values on a consistent, long-term basis. The percent RSD of the UAR values produced by the instrument was determined for a large number of analyses of NIST 4321 dilutions conducted over a period of several months under the optimized instrument conditions shown in Table 1. One analysis consists of five replicate measurements of $^{234}U^+$ ion intensity, alternating with the measurement of the $^{235}U^+$ ion intensity. The instrument software calculates a $^{234}U/^{235}U$ mass ratio from these results, along with the precision (% RSD 1-sigma) for the run based on count variations the instrument has recorded for each replicate. The precision improved when individual replicates were combined into triplicate and the error propagated (Figure 1). It is apparent that % RSD for all intensities greater than approximately 1000 cps were below 0.5% when the instrument was operating under optimized conditions.

TABLE 2. ICP/MS Instrument Operating Conditions for Dissolved U Concentration Analysis Mode

nebulizer flow	0.95 L/min
lens voltage	9 V
plasma RF power	1000 W
dead time	50 ms
sweeps	150
replicates	5
dwell time ^{238}U	100 ms
integration time ^{238}U	15000 ms
peak processing mode	averaged
scanning mode	peak hopping
detector mode	dual detector
sample introduction rate	1.2 mL/min
vacuum	$\sim 2.5 \times 10^{-5}$ Torr
spray chamber	Scott type
nebulizer	cross-flow
internal standard	2 μg/L ^{236}U

Thermal Ionization Mass Spectrometry Analysis. A set of samples possessing a range of UAR values was selected for analysis by both ICP/MS and TIMS to assess the precision and accuracy of the technique. Eleven samples were selected with UAR values ranging from 1.42 to 2.13 (measured previously by alpha-spectrometric analysis). These samples were analyzed for uranium isotopes by TIMS to a precision of 0.25% (1 sigma). For the TIMS procedure, sufficient aqueous sample to provide approximately 100 ng U was processed and loaded onto a rhenium sample filament of a Finnigan MAT 261 double filament assembly mass spectrometer. Data were collected in a series of blocks based on 10 dual scans: in sequence, $^{234}U^+$ (ion counter) was collected simultaneously for 8 s with $^{238}U^+$ (faraday), followed by collection of $^{235}U^+$ (ion counter) for 8 s. $^{234}U/^{238}U$ values were normalized to interpolated values of $^{235}U/^{238}U$, based on an assumed value of 0.007253. Data were collected until the standard deviation of the block average was 0.5% (2 sigma) or better. Ten analyses of the uraninite standard resulted in a $^{234}U/^{238}U$ ratio of 0.000551, which represents secular equilibrium, with a standard deviation of 0.2% (2 sigma).

Sample Preparation and Analysis Sequence. Water samples were filtered (0.45 μM) and acidified in the field with HNO_3 to a pH of 2 or less. The first step in the analysis sequence after the samples have reached the laboratory is the determination of their dissolved uranium concentration. This is done on the ICP/MS in elemental mode using EPA Method 200.8 (*16*) modified to use a ^{236}U spike instead of terbium as an internal standard and using instrument settings shown in Table 2. Other techniques for determination of total uranium concentration may be used, as this step is primarily used only to estimate the volume of sample needed to produce an acceptable $^{234}U^+$ ion intensity during the isotopic ratio phase of analysis.

After the U content of the samples has been measured, the volume necessary for a successful UAR determination is calculated. The injected U concentration necessary for a $^{234}U^+$ ion intensity of approximately 1000 cps is generally above 30 ppb, and an analysis can take up to 30 mL of solution. In the case of a sample found to contain 1 ppb U, for example, a 1000-mL aliquot processed to a final solution volume of 30 mL would result in an acceptable processed injection concentration of approximately 33 ppb.

The aliquot is placed in a beaker, taken to dryness on a hot plate and refluxed to dryness at least twice with reagent grade HNO_3 and 1 mL of 30% H_2O_2. The residue is refluxed to dryness twice with 8 N HCl and the residue redissolved in 5 to 10 mL of 8 N HCl and gently warmed. Much of the residue does not redissolve, so gentle disaggregation with a stirring rod is often used to ensure the acid contacts all of the solid for complete solution of the uranium as a uranyl-chloro complex ion (*17, 18*). The resulting slurry is then transferred into a 2-mL resin bed of strongly basic anion exchange medium in the Cl^- form using a 10-mL syringe with 0.45 μM filter attached to the tip. The beaker is rinsed once with another 5 mL of 8 N HCl, filtered, and added to the column. The column is then rinsed with 10 to 15 mL of clean 8 N HCl. The uranium adsorbs onto the anion-exchange resin, whereas most of the soluble cations pass through or remain in the solid residue. Several metals will also adsorb to the resin under these conditions, especially iron, but in most cases the presence of small amounts of these metals in a water sample will not interfere with the subsequent analysis and are not separated further from the uranium.

The uranium is then eluted from the resin into a clean 30-mL screw cap bottle with 10 mL of 0.1 N HCl followed by 20 mL of distilled water. This brings the solution to approximately 0.5% HCl that can then be injected directly into the ICP/MS through the ultrasonic nebulizer. This concentration process serves the dual purposes of adjusting the sample uranium concentration to optimum value and removing most constituents of the sample that would deposit on the skimmer and sampling cones, thus ensuring that many samples can be processed before having to clean the apparatus. We have run 20 samples a day for several consecutive days without the clogging problems often associated with direct injection of natural waters into the instrument. The recovery of uranium by this method, while not quantitative, is quite good (average about 85%), and no isotopic fractionation of uranium isotopes is expected as a result of the concentration procedure due to the high masses and slight relative mass differences of the uranium isotopes. The technique is easy and rapid, except for the time necessary for evaporation of the sample. It is convenient to run nine samples plus a blank through the procedure at one time and they are usually ready for analysis within 2 days. The blank is run using the same procedure, reagents, glassware, and resin as is used for the samples.

After the samples have been processed, they are ready for introduction to the instrument for measurement. The instrument is tuned and then calibrated by running a blank followed by an 80-μg/L solution of NIST 4321B Natural Uranium as a standard, which also determines the mass fractionation effect for the session. Calibration and operation are checked by re-running NIST 4321B as a sample. If the results are within ±0.002 of the known value (0.963), the samples are introduced. To monitor the overall performance of the instrument, NIST 4321B or a secondary standard calibrated against NIST 4321B is run after every third sample. If significant drift is found (usually evidenced by a UAR value different from the accepted value by equal to or more than 0.002 units on three successive replicates), the instrument is re-standardized, and the suspect results are re-computed. By periodically running the secondary standard, the instrument can be monitored to ensure optimal performance without using excessive amounts of NIST 4321B. After all samples have been run, the NIST 4321B standard is re-run several times for a final stability check.

Results

Comparison of Method with TIMS. The ICP/MS and TIMS results are shown in Table 3 and Figure 2. These samples ran at a $^{234}U^+$ ion intensity on the ICP/MS of from just over 300 cps to almost 9000 cps. The samples were either injected directly into the instrument without pretreatment or were concentrated by evaporation and ion exchange as described earlier. Results were determined using from one to nine replicates. The high intensity (concentrated) samples were run only once due to a lack of sample volume for repeated analyses, but the lower intensity (unconcentrated) samples

TABLE 3. Comparison of ICP/MS and TIMS UAR Values

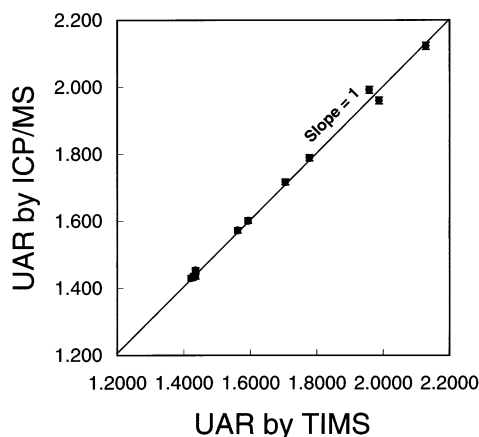| sample	U (µg/L)	TIMS UAR (±0.25%, 1 sigma)	ICP/MS UAR	no. of reps
2B-2 (4/97)	9.1	1.957	1.992±0.015	1
interstate canal	8.4	1.561	1.573±0.015	1
2B-2 (6/97)	9.3	1.705	1.717±0.009	1
2B-3	9.3	1.593	1.602±0.009	1
1D-1	12.4	2.128	2.123±0.002	1
1D-3	11.3	1.435	1.435±0.004	1
1E−1	16.9	1.987	1.960±0.005	1
Horse Creek	43.4	1.777	1.789±0.009	9
Kiowa 1−2	74.4	1.435	1.454±0.006	9
Kiowa 26−2	64.3	1.422	1.431±0.007	7
Kiowa 26−3	66.5	1.429	1.437±0.006	9

FIGURE 2. Comparison of UAR values for water samples determined by thermal ionization mass spectrometry (TIMS) and ICP/MS. Errors for TIMS analyses are 0.25% RSE, 1 sigma.

FIGURE 3. UAR determined for uranium ore from Zaire over a range of $^{234}U^+$ ion intensities determined from October to December 2000.

TABLE 4. Uranium Isotopic Activity Ratios of Natural Waters Determined by ICP/MS

sample id	type surface/ ground	U conc (µg/L)	samp vol (mL)	UAR	error (1 sigma)	% RSD
Well 6I	ground	55.5	50	1.511	0.002	0.13
Well 8G	ground	27.1	100	1.586	0.003	0.19
Well 7D2	ground	17.6	50	1.730	0.009	0.52
Pyramid Lake	surface	17.5	100	1.419	0.004	0.28
TriState Canal	surface	11.7	30	1.564	0.010	0.64
Well 1M3	ground	11.0	300	1.290	0.004	0.31
Well 7G2	ground	7.8	100	1.400	0.015	1.07
Interstate Canal	surface	7.3	300	1.562	0.003	0.19
Well 2B3	ground	7.1	300	1.554	0.004	0.26
Trout Creek	surface	2.5	1000	1.365	0.004	0.29
Well Elks	ground	1.6	500	1.239	0.005	0.40
Lake Tahoe	surface	0.9	2000	1.307	0.006	0.46
U. Truckee R.	surface	0.5	2000	1.340	0.007	0.52
Well Al Tahoe	surface	0.2	1000	1.112	0.004	0.36

were run multiple times to gain some idea of reproducibility at low $^{234}U^+$ ion intensity.

Results for the ICP/MS were excellent compared to the TIMS value of each sample, illustrating that ICP/MS has utility in determining UAR values of natural water samples. The correlation coefficient between the two data sets is 0.998. This exercise showed that ion intensities as low as 300 cps for $^{234}U^+$ are stable and sufficient for UAR determinations to precisions of ±0.5% RSD or better.

Analysis of Uranium Ore in Secular Equilibrium. A uranium ore sample from Zaire (Belgian Congo) was analyzed multiple times over a long period of time to investigate the stability of the instrument and constancy of results over a range of $^{234}U^+$ intensities. Because of the age of the ore (>500 my), the UAR should be at a secular equilibrium value of 1.000. The sample was totally dissolved, and the uranium purified on anion-exchange resin in 8 N HCL as described earlier. The uranium was diluted to give $^{234}U^+$ ion intensities of from less than 200 cps to over 10,000 cps when introduced into the instrument after optimization. The results of these analyses, run during a period from October to December 2000, are shown in Figure 3. For $^{234}U^+$ ion intensities above 1000 cps, all determinations were within ±0.5% RSD of 1.000.

Analysis of Natural Waters - - Some Examples. Results of natural waters analyzed for uranium isotopes by ICP/MS using the technique described in this paper are listed in Table 4. The samples covered a wide range of uranium concentrations. In all cases except one, the RSD of the determined UAR was below 1%, with the majority below the 0.5% target set for this technique. By simply increasing the sample volume, all analyses could have met the 0.5% RSD target.

Water was sampled from wells, lakes, and streams. All samples were freshwater except for those from Pyramid Lake,
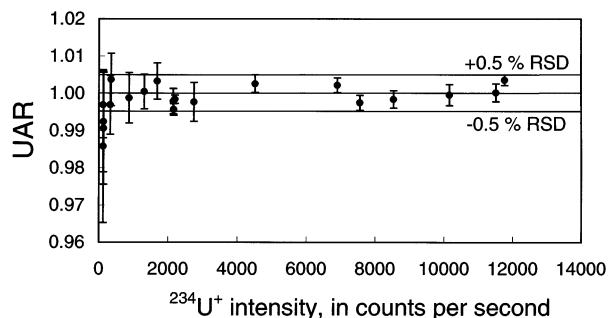
which is saline, but that presented no difficulty in the concentration/cleanup step or on introduction of the processed sample into the ICP/MS.

Water containing over 20 µg/L U can be successfully analyzed by this technique using 30- to 50-mL aliquots. Those with concentrations between 10 and 1 µg/L require 300 to 1000 mL, and those below 1 µg/L require the largest aliquot, but generally not more than two liters.

Utility of New Technique in Hydrologic Studies - - an Illustration. The results of ICP/MS uranium isotopic analyses for surface-water samples collected from the North Platte River and associated tributaries in extreme western Nebraska (*19*) are shown in Table 5. Sheep Creek and Horse Creek are tributaries of the North Platte River that enter below Henry, but above Morrill, Nebraska. On a mixing diagram, therefore, water in the North Platte River at Morrill will be a mixture of water from the North Platte River at Henry, Nebraska, and from the tributaries that add to its volume (plus any groundwater inflow, if different in uranium isotopic composition from the surface-water sources).

In June (Figure 4A) and August (Figure 4B) 1999, water in the North Platte River at Morrill, Nebraska was a combination of upstream river water (Henry) and Horse Creek water, as shown by the fact that the North Platte River at Morrill sample falls on a straight line between these two end-members. Sheep Creek, lying well off the trend line, seems to have made no contribution to the flow of the North Platte River at these times. In addition, during August 1999, water from Horse Creek appears to have had a stronger influence on the composition of water in the North Platte River near Morrill than in June, because the Morrill sample lies closer to the Horse Creek end-member in August than it does in June.

During the November 1999 sampling (Figure 4C), the isotopic composition of North Platte River at Morrill lies

TABLE 5. Results of UAR Determination of Nebraska Surface-Water Samples by ICP/MS Technique

sample location	U (μg/L)	UAR	Q (m³/sec)
June 1999			
N. Platte River near Henry	10.3	1.573 ± 0.009	131.12
Horse Creek near Lyman	17.4	1.735 ± 0.007	4.42
Sheep Creek near Morrill	16.0	1.876 ± 0.006	1.62
N. Platte River near Morrill	11.2	1.602 ± 0.004	109.30
Tri State Canal below Henry (withdrawal)			25.09
August 1999			
N. Platte River near Henry	13.0	1.554 ± 0.012	34.55
Horse Creek near Lyman	24.8	1.716 ± 0.006	2.65
Sheep Creek near Morrill	17.6	1.853 ± 0.008	0.11
N. Platte River near Morrill	21.7	1.688 ± 0.008	6.23
Tri State Canal below Henry (withdrawal)			32.00
November 1999			
N. Platte River near Henry	29.8	1.585 ± 0.005	7.42
Horse Creek near Lyman	16.9	1.844 ± 0.009	1.90
Sheep Creek near Morrill	43.6	1.737 ± 0.005	0.89
N. Platte River near Morrill	28.2	1.644 ± 0.006	12.29
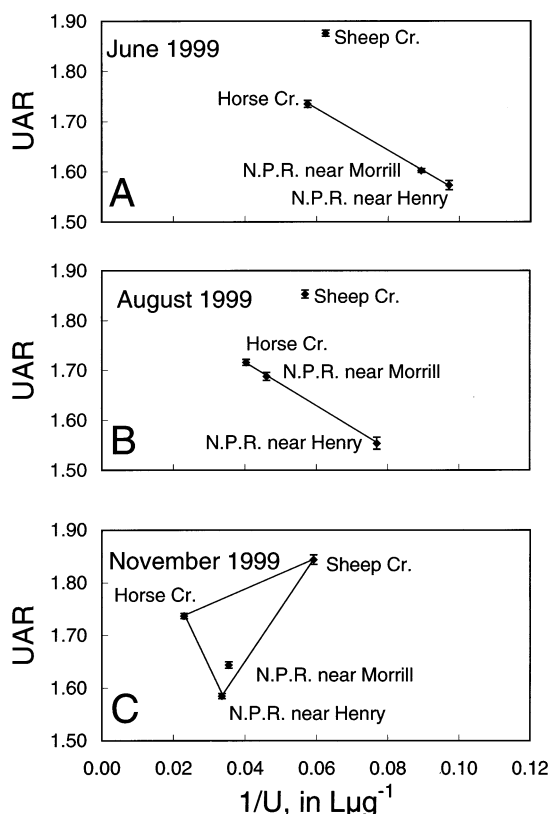
FIGURE 4. 1/U vs UAR plots for the North Platte River (NPR) and tributaries for June (A), August (B) and November (C) 1999, near Morrill, Nebraska. During June and August, the NPR apparently only received water from Horse Creek. During November, it received water from Horse Creek and Sheep Creek.

within a triangle formed by the isotopic compositions of the North Platte River at Henry, Horse Creek and Sheep Creek samples. This implies that all three end-members were contributing to the isotopic composition of the water at Morrill at this time, with both Sheep Creek and Horse Creek contributing a relatively minor amount of the entire uranium load, as evidenced by the close proximity of the Morrill sample to the point representing the isotopic composition of the North Platte River at Henry. On this type plot, however, the mixing proportions are difficult to estimate quantitatively

by visual inspection. Conservative mixing behavior of the uranium is assumed.

The observations discussed in association with Figures 4A, 4B and 4C are consistent with measured flow data determined at these corresponding sites (Table 5). In June, the North Platte River itself was the major contributor to flow down the channel between Henry and Morrill because the flow in the river was high at this time of year, although some water was diverted to irrigation canals between Henry and Morrill. By August, however, over 80% of the water flowing past Henry (now reduced from June's flow) was diverted before Morrill, making Horse Creek water a much greater percentage of the total water in the channel by the time it reached Morrill. In both cases, Sheep Creek had negligible flow to the channel (the 1.6 m3/sec value for June 1999 in table 5 is misleading, since nearly all of the water from Sheep Creek below the flow measurement point was diverted for irrigation before reaching the North Platte River (20)), in contrast to November, when a comparatively significant amount of the flow of the North Platte at Morrill was from Sheep Creek.

The utility of ICP/MS in determining water sources in a surface-water mixture is more dramatically realized when comparing the % RSD of this technique compared to alpha spectroscopy. If Figures 4A, 4B and 4C were plotted with error bars of ±5%, typical of alpha spectroscopy instead of the ±0.5% that the present method produces, it would likely be impossible to determine whether two or three component mixing was occurring in these examples because the scatter of data points would be too great for accurate plotting. The ICP/MS method described in this paper provides a rapid, accurate method of measuring uranium activity ratios in natural waters and should be a valuable tool in surface-water hydrology and environmental sciences, allowing quantitative determination of surface-water and groundwater interactions.

Interferences. In making the assumption that $[^{235}U/^{238}U]_N$ in eq 1 is constant, it is assumed that all samples will contain only natural uranium. The method should not be used, therefore, if it is likely that samples will contain either depleted or enriched uranium. We have measured the $^{235}U/^{238}U$ ratio for a number of surface- and groundwater samples and found that the ratio is as expected. It is further noted that in the comparison of samples using TIMS and ICP/MS, no evidence was seen to suggest that the assumption is not valid. It is unlikely that either depleted or enriched uranium contamination will be encountered in samples from most environments. However, in areas where such releases are known or suspected to have occurred, a measurement of the $^{235}U/^{238}U$ ratio by the ICP/MS could easily be made on each sample to determine if contamination had occurred and correct for it by substituting the correct value of $^{235}U/^{238}U$ into eq 1.

Acknowledgments

Literature Cited

(1) Osmond, J. K.; Ivanovich, M. In *Uranium-Series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences*; Ivanovich, M., Harmon, R. S., Eds.; Clarendon Press: Oxford, 1992; pp 259−289.

(2) Osmond, J. K.; Cowart, J. B. In *Uranium-Series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences*; Ivanovich, M., Harmon, R. S., Eds.; Clarendon Press: Oxford, 1992; pp 290−333.

(3) Cherdyntsev, V. V. *Uranium-234*; translated from Russian by Israel Program for Scientific translation, Keter Press: Jerusalem, 1971; 234 pp.

(4) Turner, P. J.; Mills, D. J.; Schroder, E.; Lapitajs, G.; Jung, G.; Iacone, L. A.; Haydar, D. A.; Montaser, A. In *Inductively Coupled Plasma Mass Spectrometry*; Montaser, A. Ed.; Wiley-VCH: New York, 1998; pp 421−501.

(5) Hollenbach, M.; Grohs, J.; Kroft, M.; Mamich, S. In *Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations*; Morrow, R. W., Crain, J. S., Eds.; American Society for Testing and Materials, ASTM STP 1291: West Conshohocken, Pa, 1995; pp 99−115.

(6) Boulyga, S. F.; Becker, J. S. *Fresenius J. Anal. Chem.* **2001**, *370*, 612.

(7) Heumann, K. G.; Gallus, S. M.; Radlinger, G.; Vogl, J. *J. Anal. Atomic Spectrometry* **1998**, *13*, 1001.

(8) Becker, J. S.; Dietze, H. J. *J. Anal. Atomic Spectrometry* **1997**, *12*, 881.

(9) Shen, C.; Edwards, R. L.; Cheng, H.; Dorale, J. A.; Thomas, R. B.; Moran, S. B.; Weinstein, S. E.; Edmonds, H. N. *Chemical Geology* **2002**, *185*, 165.

(10) Becker, J. S.; Dietze, H. J. *Fresenius J. Anal. Chem.* **1999**, *364*, 482.

(11) Bolin, R. N. In *Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations*; Morrow, R. W., Crain, J. S., Eds.; American Society for Testing and Materials, ASTM STP 1291: West Conshohocken, Pa, 1995; pp 116−127.

(12) Russ, G. P.; Bazan, J. M. In *Applications of Inductively Coupled Plasma Mass Spectrometry to Radionuclide Determinations*; Morrow, R. W.; Crain, J. S., Eds., American Society for Testing and Materials, ASTM STP 1291: West Conshohocken, Pa, 1995; pp 131−140.

(13) Ketterer, M. E.; Khourey, C. J. In *Applications of Inductively Coupled-Mass Spectrometry to Radionuclide Determinations: Second Volume*; Morrow, R. W., Crain, J. S. Eds.; American Society for Testing and Materials, ASTM STP 1344: West Conshohocken, Pa, 1998; pp 120−136.

(14) Browne, E.; Firestone, R. B. *Table of Radioactive Isotopes*; John Wiley and Sons: New York, 1982.

(15) National Institute of Standards and Technology. *Standard Reference Material 4321B Certificate and Notes*: 1992.

(16) *Methods for the Determination of Metals in Environmental Samples- Supplement 1*; U.S. Environmental Protection Agency, 1994; EPA-600/R-94−111.

(17) Lally, A. E. In *Uranium-series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences*, 2nd ed.; Ivanovich, M.; Harmon, R. S., Eds.; Clarendon Press: Oxford, England, 1992; pp 95−126.

(18) Kraus, K. A.; Nelson, F. In *Proc. Int. Conf. Peaceful Uses of Atomic Energy, Geneva, 1955*; **1956**, *7*, 113−125.

(19) Böhlke, J. K.; Verstraeten, I. M.; Kraemer, T. F., manuscript in preparation.

(20) Verstraeten, I. M., personal communication.